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PRODUCTION OF CO($A^3\pi$) AND OTHER METASTABLE FRAGMENTS BY ELECTRON IMPACT DISSOCIATION OF CO_2*

BY

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Abstract

The dissociative excitation of $CO(a^3\Pi)$ and other metastable fragments such as $O(^5S^0)$ produced by electron impact on CO_2 has been investigated from threshold to 50 eV. The observed threshold for $CO(a^3\Pi)$ production at (11.9 ± 0.5) eV was near the minimum required energy of 11.5 eV. Assuming an isotropic distribution of $CO(a^3\Pi)$ fragments after dissociation, and cross section for dissociative excitation of $CO(a^3\Pi)$ from CO_2 was found to be about $3.6 \times 10^{-17}cm^2$ at 20 eV which is 3 times smaller than the maximum cross section for the direct excitation of $CO(a^3\Pi)$ from CO. We also used our time of flight data to infer a value for the $CO(a^3\Pi)$ dissociative excitation cross section from Ajello's relative cross section measurements (1971 A) and we obtained a slightly lower value of $1.6 \times 10^{-17}cm^2$ at 20 eV. These experiments imply a maximum cross section value of $(4.1 \pm 3.0) \times 10^{-17}cm^2$ at 27 eV. The differential cross section for the dissociative excitation of $CO(a^3\Pi)$ at right angles to the electron beam was found to be $d\sigma/d\Omega = (3.0 \pm 2.2) \times 10^{-18}cm^2/sterad$ at an energy of 20 eV.

INTRODUCTION

Recent observations of the intense CO Cameron band emission in the upper Martian atmosphere by Mariner 6 and 7 (Barth et al., 1969; Barth et al., 1971) has generated a renewed interest in the dissociative excitation of CO_2 by both electron impact and photodissociation. In order to determine the role played by these processes, it is necessary to know the absolute collision and absorption cross sections. To this end we have studied the production of metastable fragments by electron impact on CO_2 in an attempt to arrive at an absolute cross section for the production of the $CO(a^3\Pi)$ state.

APPARATUS

The pulsed electron beam time of flight apparatus used in this experiment and its modes of operation have been described in detail elsewhere [Borst and Zipf, 1971 A; 1971 B]. Two major modifications have been carried out. Firstly, voltage programming the electron energy to sweep concurrently with the multiscaler has permitted signal averaging of excitation functions and has significantly improved the signal to noise ratio in the primary data.

Secondly the metastable detector was rearranged so that several different metal surfaces could be used as Auger detectors. Electrons which were ejected from a metal surface by incident metastable fragments were accelerated toward an electron multiplier. The metal surface was positioned at an angle of 45° with respect to the incoming metastables, and was at an effective distance of 20.0 cm from the center of the collision

chamber. The metals used in this experiment were tungsten and magnesium. The solid angle subtended by the detector surface at the center of the collision chamber was 0.007 sterad at an angle of 90° with respect to the electron beam. The electron beam pulse was typically 10 μsec wide with a repetition rate of 2×10^2/sec.

RESULTS AND DISCUSSION

As in previous studies [Freund and Klemperer, 1967, and Clampitt and Newton, 1969] metastable CO_2 molecules were not observed in this experiment. The excitation function [Fig. 2] for the production of the relatively slow metastable fragments [Structure A, Fig. 1] exhibited an appearance potential of 11.9 ± 0.5 eV [Fig. 2]. This threshold is to be compared to Freund and Klemperer's [1967] value of 12 - 15 eV and Clampitt and Newtons's [1969] value of 11.0 ± 0.6 eV. Our threshold value is in agreement with the observations of Freund and Klemperer. The threshold reported by Clampitt and Newton probably corresponds to the detection of $O(^1S)$ atoms as was pointed out by McConnell and McElroy [1970]. Our detector, like that of Freund's, was not sensitive to $O(^1S)$ atoms. Accurate determination of the threshold in our experiment was made difficult by such effects as the slight non-instrumental curvature of the excitation function at threshold and poor signal to noise ratio at threshold. Freund and Klemperer [1967] showed that the metastable fragment is polar and hence probably is $CO(a^3\Pi)$. The excitation process that we are observing is most likely,

$$e + CO_2(\tilde{X}\ ^1\Sigma_g^+) \rightarrow CO_2^* + e$$

$$CO_2^* \rightarrow CO(a^3\Pi) + O(^3P) \qquad (1)$$

which has a threshold of 11.5 eV. Our threshold determination does not completely rule out a cascade process where

$$e + CO_2(\tilde{X}\ ^1\Sigma_g^+) \rightarrow CO_2^* + e$$
$$CO_2^* \rightarrow CO(a'\ ^3\Sigma^+) + O(^3P) \qquad (2)$$

and

$$CO(a'\ ^3\Sigma^+) \rightarrow CO(a^3\Pi) + h\nu \qquad (3)$$

The end result in either case is the production of $CO(a^3\Pi)$.

The mean energy of the $CO(a^3\Pi)$ molecules near threshold was observed to be about 0.08 eV which corresponded to a total fragment mean kinetic energy of about 0.2 eV. This is in general agreement with the observations of Freund and Klemperer [1967] but in disagreement with the work of Clampitt and Newton [1969] who observed a total fragment mean kinetic energy of 0.7 eV. Again this discrepancy could be due to the fact that Clampitt and Newton were detecting a small percentage of very energetic $O(^1S)$ along with the $CO(a^3\Pi)$; this was not possible in our experiment. The low velocity tail [Structure A. Fig. 1] corresponds to the production of some $CO(a^3\Pi)$ molecules with virtually no excess kinetic energy.

Other Sources of $CO(a^3\Pi)$

As we went to higher electron impact energies we produced $CO(a^3\Pi)$ molecules from processes other than those mentioned previously. It is possible that cascade processes similar to (3) and (4) involving higher lying triplet levels of the CO molecule contributed to the production of $CO(a^3\Pi)$

molecules. Another excitation process may have been

$$e + CO_2(\tilde{X}\ ^1\Sigma_g^+) \rightarrow CO_2^* + e$$
$$CO_2^* \rightarrow CO(a^3\Pi) + O(^3S) \qquad (4)$$

which has a minimum threshold of 21.0 eV.

A detailed study of high resolution time of flight curves revealed the development of a new structure which manifested itself as a high velocity tail on structure A [Fig. 1] at about 22 eV. This new source of $CO(a^3\Pi)$ is evident in Fig. 2 in both excitation functions A and B since the TOF spectra for process (4) falls into both the slow and fast portions of the TOF spectrum which the excitation functions represent. The $CO(a^3\Pi)$ molecules from process (4) are visible as additional structure to excitation function A at 21.6 ± 1 eV and as a threshold in excitation function B at 22.1 ± 1 eV. These energy thresholds are in agreement with the minimum threshold of 21.0 eV for process (4) and furthermore are consistent with the thresholds for $O(^3S)$ production of 21.0 ± 2 eV and 23 eV observed by Ajello [1971 B] and Mumma [1970], respectively.

To determine if all the metastable fragments in structure A [Fig. 1] were $CO(a^3\Pi)$ molecules, the excitation function A [Fig. 2] was observed using four different detector surfaces. The efficiency γ_m for Auger ejection of electrons by $CO(a^3\Pi)$ from these different surfaces varied by as much as a factor of 5. The four surfaces were a Cu-Be nude dynode, two contaminated tungsten surfaces for which γ_m differed by a factor of 2 and a contaminated magnesium surface. It is known [Clampitt and Newton, 1968] that the apparent

excitation function due to an incident metastable flux consisting of a mixture of different metastable states has a different shape when detected with surfaces having different work functions. Indeed γ_m is a sensitive function of the difference between the work function of the surface and the metastable energy level. All the surfaces used in this experiment yielded quite similar excitation functions leading us to conclude that excitation function A represents the production of $CO(a^3\Pi)$ from electron impact on CO_2.

Determination of $CO(a^3\Pi)$ Differential Cross Section

To determine the differential cross section for the dissociative excitation of $CO(a^3\Pi)$, we also observed the excitation function [Borst and Zipf, 1971 B] on the same TOF apparatus for the direct process

$$e + CO(X^1\Sigma^+) \rightarrow CO(a^3\Pi) + e \,. \tag{5}$$

Using Ajello's [1971 A] peak cross section for this process [$1.1 \times 10^{-16} cm^2$ at 10.4 eV] and our knowledge of the relative peak production rates of $CO(a^3\Pi)$ from CO and CO_2 we arrived at a differential cross section of

$$\left(\frac{d\sigma}{d\Omega}\right)_{90^\circ} = 3 \times 10^{-18} cm^2/sterad \tag{6}$$

at 20 eV. A lifetime of 1 msec [Borst and Zipf, 1971 B] was used to correct the cross section measurement for the radiative decay of the $CO(a^3\Pi)$ in flight. This correction is relatively insensitive to the specific lifetime value used. Choosing a longer lifetime would result in at most a 10% change in the relative signal of $CO(a^3\Pi)$ from CO and CO_2. At the same time it should

be noted that the absolute magnitude of this dissociative excitation cross section does depend linearly on Ajello's [1971 A] direct excitation cross section and that Ajello's cross section in turn depends linearly on the lifetime of the CO($a^3\Pi$) state. Ajello used a value of 1 msec [Borst and Zipf, 1971 B].

There has been a great deal of discussion of the CO($a^3\Pi$) lifetime in the literature recently. Borst and Zipf [1971 B] have discussed the early lifetime work on this state at length. More recently Lawrence [1971] has reported a lifetime of 7.5 msec for this state while Slanger and Black [1971] found a value of 5 msec. It must be said at the outset in a discussion of the CO($a^3\Pi$) radiative lifetime that it is misleading to assume that a complex electronic band system such as the $a^3\Pi \leftrightarrow X^1\Sigma^+$ transition has a single-valued lifetime. As a matter of fact there is an entire manifold of different radiative lifetimes, one for each rotational sublevel [Shemansky, 1969]. Recently Fairbairn [1971] discussed this lifetime variation with J and spin substate Σ in connection with an absorption measurement. James [1971] has also dealt with this problem in a theoretical calculation of the f values and lifetimes. Although it is convenient experimentally to measure some "average" lifetime for this system, it must not be forgotten that the end result obtained depends on just how the rotational and spin states are populated.

At low rotational levels ($J < 16$) the $^3\Pi_1$, levels exhibit shorter radiative lifetimes and larger line strengths than the corresponding $^3\Pi_0$ and $^3\Pi_2$ levels [Hexter, 1967; Fairbairn, 1970]. In electron impact experiments such as those of Ajello [1971 A] and Borst and Zipf [1971 B] where CO at room temperature (300°K) is excited, the $^3\Pi_1$ levels will be preferentially excited. In experiments involving high pressures where the CO($a^3\Pi$) molecule

undergoes several collisions before radiating we would expect the populations of the spin states to equilibriate resulting in a longer observed lifetime; quenching, of course, further complicates the analysis of these afterglow experiments. The fact that the result of Borst and Zipf [1971 B] (τ = 1 msec) measured in a low pressure environment falls on the low side of the recent lifetime measurements made in high pressure environments (Slanger and Black [1971] (5 msec) and Lawrence [1971] (7.5 msec)) suggests that this is indeed the case.

These considerations argue that Ajello used the appropriate lifetime in normalizing his results [Ajello, 1971 A]. Choosing a lifetime of 7 msec would have resulted in a cross section for process (5) of $7.7 \times 10^{-16} cm^2$ and the differential cross section (6) would have become $2.1 \times 10^{-17} cm^2$/sterad. These would be remarkably large values.

It has been assumed in arriving at this differential cross section that the effective Auger efficiency for detecting the $CO(a^3\Pi)$ has been the same for direct and dissociative excitation. This is equivalent to assuming that the mean energy carried in vibrational energy is the same for both processes provided that the variation of γ_m with metastable energy is quasi-linear over this narrow range. This is not an unreasonable assumption despite the fact that Barth et al. [1971] reported that the vibrational population distribution of dissociative excited $CO(a^3\Pi)$ is different from that of directly excited $CO(a^3\Pi)$. As a matter of fact the mean vibrational energy calculated based on the populations Barth reports and the mean energy calculated based on the Franck Condon factors of Nicholls [1962] are the same to within 0.05 eV. Differences in rotational distributions should have an unnoticeable effect on the effective γ_m for detecting $CO(a^3\Pi)$ because of the small energies involved.

The uncertainty in our value for the cross section arising from experimental errors in the actual relative intensity measurements are deemed to be less than 30%. In view of this we feel that the uncertainty in our absolute cross section for dissociative excitation of $CO(a^3\Pi)$ is determined primarily by the uncertainty in Ajello's [1971 A] cross section for process (5) which is a factor of 2.

Determination of $CO(a^3\Pi)$ Total Cross Section

Examination of Ajello's [1971 B] excitation function for the dissociative excitation of the Cameron bands by electron impact on CO_2 reveals a steadily increasing curve with a broad maximum centered about 90 eV. This is to be compared to the relatively flat behavior of excitation function A [Fig. 2] above 20 eV with the maximum at 27 eV. Ajello's excitation function is 30% larger at its peak than at 27 eV. If we assume that at 20 eV we have isotropic scattering, we are in a position to renormalize Ajello's excitation function at low energies.

At 20 eV Ajello's [1971 B] emission cross section is $6.1 \times 10^{-18} cm^2$ where he assumed a thermal velocity distribution of the $CO(a^3\Pi)$ fragment. The slow metastable CO molecules [Structure A, Fig. 1] have a mean velocity 2.7 times a thermal mean velocity. This yields an absolute emission cross section for the slow fragments of

$$\sigma \simeq 1.6 \times 10^{-17} cm^2 \qquad (7)$$

at 20 eV. This can be compared to the differential cross section (6) derived earlier. Assuming isotropic scattering with respect to the scattering angle

results in an excitation cross section of

$$\sigma \simeq 3.6 \times 10^{-17} cm^2 \qquad (8)$$

at 20 eV. In arriving at the cross section values (7) and (8) we assumed isotropic scattering. Strictly speaking we only assumed that the velocity distribution of $CO(a^3\Pi)$ was unaltered in arriving at cross section (7). One might expect as we go to higher energies that the strong angular dependencies in the differential cross section would disappear since more repulsive states in CO_2 are being excited. But the discrepancy in shape between our excitation and that of Ajello's discussed above would argue that at high energies the scattering is not isotropic. It is difficult to assess precisely the uncertainty in our total cross sections which would result from anisotropy since the angular distribution has not been examined yet. We estimate here a factor of two uncertainty due to the assumption of isotropy.

In arriving at cross section (7) we used Ajello's [1971 B] cross section which he arrived at using a lifetime of 1 msec [Borst anf Zipf, 1971 B] to account for those $CO(a^3\Pi)$ molecules which left his field of view before radiating. As has been discussed previously the "average" lifetime for the $CO(a^3\Pi)$ depends dramatically on the rotational level population and spin state populations. There is no reason to expect these populations to be the same for directly excited $CO(a^3\Pi)$ and dissociatively excited $CO(a^3\Pi)$. Indeed Mumma et al. [1971] have observed non-thermal rotational distribution in $CO(A^1\Pi)$ produced by dissociative excitation of CO_2 by electron impact. If the spin states are more or less equally populated and the rotational distribution is skewed toward higher rotational numbers the net effect would be a longer $CO(a^3\Pi)$

lifetime. This would result in a corresponding increase in cross section (7) bringing it into closer agreement with cross section (8). The cross sections (7) and (8) are to be compared with an order of magnitude estimate of the maximum cross section of $2 \times 10^{-16} cm^2$ at 40 eV by Freund and Klemperer [1967]. The reason for the large disagreement is not understood. McConnell and McElroy [1970] arrived at a maximum cross section of $8 \times 10^{-17} cm^2$ for the production of $CO(a^3\Pi)$ based on a theoretical paper by Strickland and Green [1969].

$O(^5S)$ Cross Section

We observed that as the detector surface was changed the peak height of structure B [Fig. 1] remained relatively unchanged while that of structure A changed dramatically. This implied that structure B was composed in part of higher lying metastable states and possibly Rydberg states of C, O, and CO. The change in slope in excitation function A [Fig. 2] around 29 $\pm$ 2 eV probably corresponds to the dissociative process

$$\begin{aligned} e + CO_2(\tilde{X}^1\Sigma_g^+) &\rightarrow CO_2^* + e \\ CO_2^* &\rightarrow O(^5S) + O(^3P) + C(^3P) \end{aligned} \qquad (9)$$

which has a minimum threshold of 25.7 eV. Dissociative production of $O(^5S^0)$ has been observed by Ajello [1971 B] with a threshold of 27 $\pm$ 2 eV. Assuming that excited oxygen atoms are being observed, then structure B [Fig. 1] corresponds to atomic fragments with a sum total kinetic energy of at least 3 eV. Ajello [1971 B] observed a cross section for the production of $O(^5S^0)$

atoms approximately 0.95 times the $O(^3S)$ cross section [$7.6 \times 10^{-19} cm^2$ at 100 eV] assuming a thermal velocity distribution. If we assume that structure B [Fig. 1] is largely due to the excitation of $O(^5S)$ atoms then our measurements imply a mean velocity for these oxygen atoms 9 times the mean thermal velocity. Multiplying Ajello's cross section by 9 to compensate for excited atoms which left his field of view before radiating yields an emission cross section

$$\sigma \approx 6.8 \times 10^{-18} cm^2 \qquad (10)$$

at 100 eV for the production of $O(^5S^0)$ atoms.

SUMMARY

We have excited the $CO(a^3\Pi)$ Cameron band system with high efficiency by electron impact dissociation of CO_2 near the minimum possible threshold of 11.5 eV and up to 50 eV. We have further studied energy spectra of the resulting $CO(a^3\Pi)$ and other metastable fragments. We obtained a cross section of about $3.6 \times 10^{-17} cm^2$ for the dissociative excitation of $CO(a^3\Pi)$ at 20 eV assuming an isotropic angular distribution of metastables after dissociation; this result is probably accurate to within a factor of 2. A maximum cross section occurring at higher energies was not observed in contrast to Ajello's measurements. However, interpretation of the high energy domain was rendered difficult because of the presence of metastable fragments other than $CO(a^3\Pi)$, e.g. $O(^5S)$. The above cross section was deduced by comparing $CO(a^3\Pi)$ signals obtained in <u>dissociative</u> excitation with those for <u>direct</u> excitation using Ajello's cross section for <u>direct</u> excitation of $CO(a^3\Pi)$ from $CO(X^1\Sigma^+)$. We further applied our time-of-flight measurements

of non-thermal CO($a^3\Pi$) fragments to Ajello's optical measurements of Cameron bands produced in <u>dissociative</u> excitation from CO_2 and inferred a cross section of $1.6 \times 10^{-17} cm^2$ at an energy of 20 eV. The two values of $3.6 \times 10^{-17} cm^2$ and $1.6 \times 10^{-17} cm^2$ thus obtained agree well within the limits of error.

We can conclude that the cross section for the dissociative excitation of CO($a^3\Pi$) by electron impact on CO_2 is large. However, the probable errors in these measurements are also large so that some care should be exercised in applying these results to the analysis of planetary atmospheres. This suggests that it is premature to conclude that electron impact dissociative excitation is the primary source of the Cameron bands in the Martian dayglow.

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Figure Captions

Figure 1 Multi-channel analyzer plot of the time-of-flight distribution of metastable fragments resulting from the dissociation of CO_2 by 38.5 eV electrons. The channel width was 10 μsec. Peak heights of A and B depended on the detector surface used.

Figure 2 Excitation functions for the dissociative excitation of metastable fragments. Curves A and B correspond to the excitation of structures A and B in Fig. 1, respectively. In an attempt to separate the partially resolved structures, the following counting windows were used: curve A, 145 to 1000 μsec with a 50 μsec gun pulse and curve B, 25 to 55 μsec with a 10 μsec pulse. At an energy of 50 eV with a tungsten surface, the ratio of curve A to curve B was 2.74. Curve A corresponds mainly to $CO(a^3\Pi)$ where as curve B was caused mainly by $O(^5S)$.

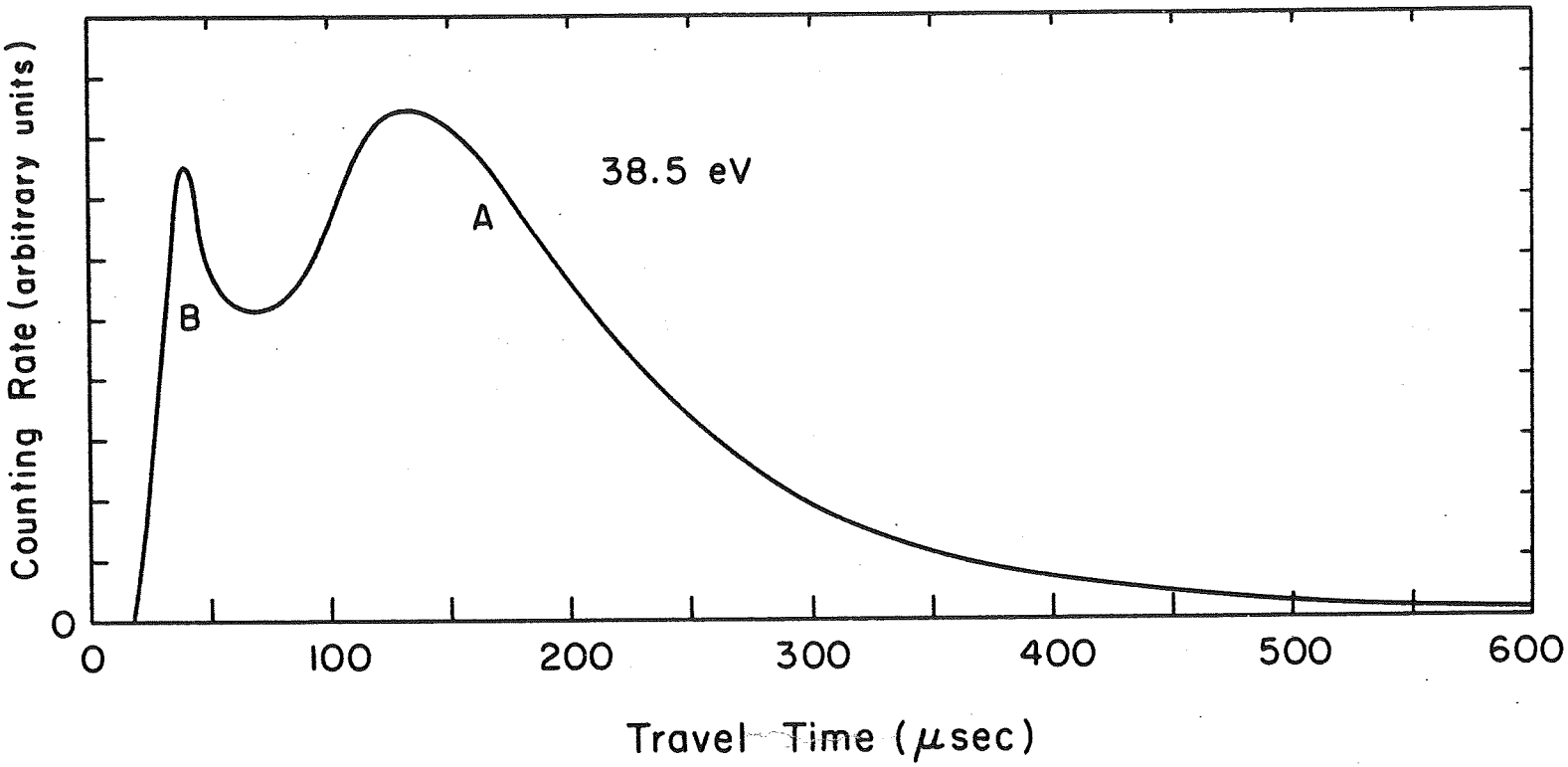
Counting Rate (arbitrary units)
38.5 eV
A
B
0
0
100
200
300
400
500
600
Travel Time (μsec)

Figure 1

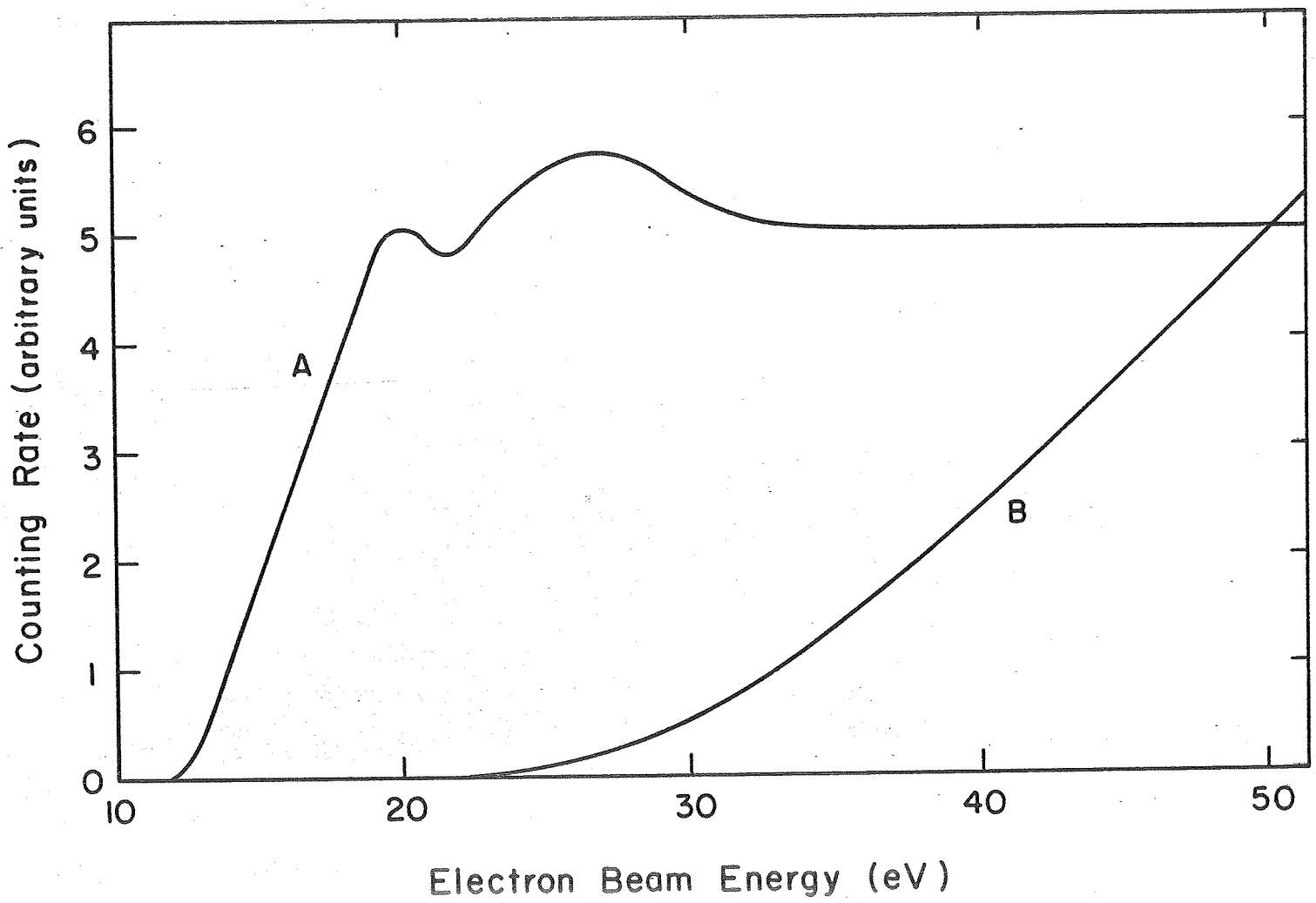
Counting Rate (arbitrary units)
0
1
2
3
4
5
6
10
20
30
40
50
Electron Beam Energy (eV)
A
B

Figure 2